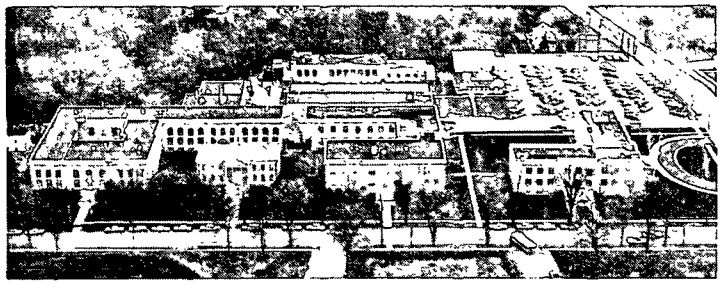

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FAST REACTIONS IN ALKALINE PULPING. II. THE PEELING REACTION

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INTRODUCTION

In the past, the stepwise removal of end units from water-soluble carbohydrates of short chain length had been studied in alkaline systems at low temperatures where the rate of reaction was relatively slow and easily measured. This "peeling" reaction was then suggested to explain yield losses in polysaccharides at higher temperatures, i.e., for cellulose in alkaline pulping processes. However, there has been no real evidence that the same reaction occurred at both low and high temperatures.

Now, with the aid of a flow reactor, the peeling reaction has been studied at temperatures up to 170°C for the disaccharide, cellobiose, and it has been found that this is the same type of reaction that occurs at lower temperatures. The same type of reaction products have been found for a temperature range from 60 to 170°C. Reaction times decreased rapidly with increasing temperature, to about 10 milliseconds at 170°C.

The reaction rates seem to be constant at a given temperature for alkali concentrations above 0.1N sodium hydroxide, and unaffected by addition of sulfide, in concentrations ordinarily used in the kraft pulping process. The rates found at the higher temperatures are of the same order as those found indirectly for polysaccharides, and justify the existence of a peeling process for the latter type of compound.

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Fast reactions in alkaline pulping. II.

The peeling reaction

John W. Green, Irwin A. Pearl, and Fred C. Haigh

Abstract

The alkaline degradation of cellobiose in aqueous sodium hydroxide has been studied up to 170°C. Glucose is found, as well as isosaccharinic acid, as a product of peeling. The rate of the reaction bears a linear relationship to temperature. It is concluded that the peeling reaction, previously observed at lower temperatures, also exists at higher temperatures under pulping conditions. The rate of reaction is constant with respect to alkali concentration above 0.5N NaOH, and is not affected by sulfidity.

The losses in polysaccharide yields in alkaline pulping have received much attention; the rates of removal of carbohydrate material have been determined and many efforts have been spent to prevent this by blocking of end groups (1). The carbohydrate removal has been ascribed to a "peeling" reaction, the breaking of a glycosidic unit adjacent to an end unit containing a carbonyl group. This concept of peeling was first described by Corbett and Kenner (2) for the degradation of disaccharides and oligosaccharides up to a DP = 4; the reactions were carried out in mild alkali at low temperatures, and it was demonstrated that each peeling reaction gave a new oligosaccharide of DP = n-1. The reaction was studied in detail by MacLaurin and Green (3) for cellobiose, a disaccharide, in N NaOH at 22°C.

The reactions studied at low temperatures are very slow, with half-lives of the order of 20 to 30 hours. In the reactions with polysaccharides at 100° and 170°C the reactions are much faster and only the loss in yield, the peeling of many units from a chain, has been determined. No attempt has been made to study the peeling reaction with simple carbohydrates at higher temperatures; the high rates of reaction have prevented such study. Lindberg, et al. (4) reported the rates of disappearance of disaccharides in dilute alkali at 60° and 75°C but no attempt was made to demonstrate the formation of monosaccharides as a product of peeling.

Recently we have constructed a flow reactor (5) which is capable of handling very short reaction times at higher temperatures under pressure. This apparatus has been applied to the alkaline degradation of cellobiose in aqueous sodium hydroxide and we have found that glucose is

formed, as well as isosaccharinic acid, as a product of peeling at temperatures up to 170°C, and that the rate of the reaction (disappearance of disaccharide) bears a linear relationship to temperature over a range from 60° to 170°C. This can be considered as proof that the peeling reaction, observed at lower temperatures, also exists at higher temperatures under pulping conditions. The rate of reaction is constant with respect to the alkali concentration above 0.5N NaOH, and is not affected by sulfidity. An example of such a reaction at short time intervals is shown in Fig. 1.

[Fig. 1 here]

EXPERIMENTAL

Operation of the Flow Reactor

Solutions of sugars and alkali were made up in boiled and cooled water to prevent formation of air bubbles in the heating coils of the reactor. Concentrations were twice those of the final mixed reaction solutions, as equal volumes of each are forced through the reaction coil. The syringes were rinsed three times with the respective solutions to insure even concentrations. Cyclohexyl β-D-glucoside was added to the sugar solution as an internal standard when subsequent analyses were done by gas chromatography.

The reactor was operated as described elsewhere (5). The reaction solutions were quenched with cold aqueous boric acid. For 2N NaOH a concentration of 0.5M boric acid gave a quench solution of pH 9.5 to 10; for more dilute alkali the boric acid was diluted to maintain the above pH range. With the given volumes of heating and reaction coils used in the reactor, usually about 14 ml of reaction solution was mixed

with 100 ml of boric acid.

The flow rate of liquid through the reaction coil was determined from the data on the oscillograph recorder, and the reaction times calculated from this flow rate and from the volume of the reaction coil (5). These reaction times are given in the figures and in Table I.

[Table I here]

Borohydride Reduction of Quenched Solutions

These solutions (about 115 ml) were immediately treated with 200 mg of sodium borohydride, added with stirring, to reduce the mono- and disaccharides to the alcohols. The amount of this reagent is about 4X the weight of the original disaccharide in the solution. The concentration is about 2 mg/ml and seems to effect a complete reduction when the solutions are left overnight. McCready and Duclay (6) have recommended a minimum concentration of 5 mg/ml for complete reduction in 30 minutes.

Aliquots (1 ml) of these solutions were taken for the colorimetric (PSA) method.

When the gas chromatographic (GLC) method was used, borate was removed first. The solutions were stirred with an excess of Amberlite IR-120 cation-exchange resin; the final pH of the solutions was 3 to 3.5. Very little hydrogen was evolved at this stage. Most of the reagent had either reacted or decomposed in the buffer solution during the overnight period. Appreciable hydrogen was evolved if a 3-hr reduction period was used.

The mixture was filtered and the solution concentrated at 50°C to dryness, then concentrated twice with methanol (100 ml) to remove

boric acid. The residue was dissolved in water (100 ml) and run through a column of Amberlite MB-3 mixed bed resin (30 ml) to remove organic acids. The column was washed with water (100 ml) and the combined solutions divided into two portions; one is set aside as a reserve.

Acetylation of the Sugar Alcohols

One portion of the above solution was concentrated to dryness, dried 15 min at 105°C, cooled and treated with pyridine (6 ml) and acetic anhydride (5 ml) for 15-20 hr at room temperature. The mixture was then poured into ice water (60 ml), stirred 15 min, extracted with chloroform (3 x 20 ml) and the latter washed successively with 1N HCl (60 ml), 0.1N HCl (60 ml) and water (3 x 60 ml). The organic layer was dried over sodium sulfate, concentrated to dryness, and the residue dissolved in 5 ml acetone.

Gas Chromatographic Analysis (GLC)

The acetone solution (1 to 5 µl) was injected on a 5% SE-30 column (5 ft x 1/8 inch, on 60/80 acid-washed DMCS Chromosorb W), programmed at 4/min from 175° to 275°C and held. The two peaks analyzed were hexitol acetate (glucitol and mannitol) at 6.6 min retention time, and dodecitol acetate (cellobiitol and glucosyl-mannitol) at 22 min. The internal standard, cyclohexyl β-D-glucoside acetate, had a retention time of 10.5 min. On-column injection was normally used.

Glucosyl-mannitol acetate was made by the borohydride reduction of 4-O-β-D-glucosyl-mannose (3) and subsequent analysis.

Colorimetric (PSA) Method for Disaccharides

This is the method of Painter (7). The color developed by the phenol-sulfuric acid reagent was measured at 490 nm. No internal standard was possible in this method, and a dilution factor for the amount (about 14 ml) of reaction solution in the final quenched solution was used. Such a factor was obtained by blank runs in the flow reactor, with water instead of boric acid as a quench reagent, and titration of the amount of alkali in the resulting quench solution.

Aliquots (1 ml) are analyzed and the results compared with a calibration curve obtained with samples containing the same amount of borate buffer.

The PSA method is a much faster method than the GLC method; with the latter method, 3 working days are required to work up 4 samples. However, the PSA method is less accurate and semilog plots often had to be corrected to give the proper zero time intercept (see Table I and Fig. 2).

[Fig. 2 here]

DISCUSSION OF RESULTS

The data for reaction runs from 60 to 170°C are given in Table I. The data for 60 and 75°C were obtained in a simple glass flow reactor that served as a prototype for the pressurized flow reactor.

First-order plots were obtained for all reactions with an excess of alkali present. The accuracy of the data was much better when obtained by gas chromatography than by the colorimetric method. The rate at 120°C

was found to level off when the alkali was increased to 0.5N (see Fig. 2). The sulfidity of the solution did not affect the rate of reaction (see Fig. 3); the effective alkali is the important factor.

[Fig. 3 here]

The kinetics were expressed as half-lives of the original disaccharide (see Table II). This parameter was used, rather than rate constants. The concept of a half-life was more meaningful in the design and operation of the flow reactor than a rate constant.

[Table II here]

Plots of the half-lives against the reciprocal of the absolute temperature are roughly linear (Fig. 4 and 5) and show the common relationship of the reactions over a wide temperature range. In Fig. 5 the half-life at 170°C is not shown. The extrapolated value is 7.5 milliseconds, the calculated value is 11.6 milliseconds.

[Fig. 4 and 5 here]

In Fig. 6 are shown data for the time intervals below 15 milliseconds; here it can be seen that the time of mixing of the reactants is an appreciable factor, especially in the 1-millisecond range. The limitations of the reactor are also shown in Fig. 7; the semilog plot shows that the reaction in strong alkali at 170°C is over 50% complete at a calculated reaction time of zero. This zero time intercept shows that appreciable reaction is occurring in the mixer area, and the volumes of the reaction coils (used to calculate reaction times) are not correct. The efficiency of mixing is a function of the flow rate (8). To keep the extent of reaction in the mixer region a constant factor, the flow

rate has been kept constant (Fig. 7) and the volumes of the reaction coils varied.

[Fig. 6 and 7 here]

CONCLUSIONS

The kinetics for the breaking of a glucosidic bond in a disaccharide by peeling are of the same order of magnitude as those found for similar bonds in polysaccharides (1) at elevated temperatures. The rates found at 60° and 75°C are much higher than those found by Lindberg, et al (4) due to the higher concentrations of alkali used in this work.

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Table I. Data for Flow Reactor Runs

Temp., °C	NaOH concn.	Reaction time, millisec	Cellobiose C/C_o	Glucose C	Volume of reaction coil, ml	Anal. method
60	2N	68,000	0.905	0.025	5	GLC
		206,000	0.760	0.125		
		331,000	0.678	0.20		
		532,000	0.453	0.31		
60	2N	59,000	0.937	0.040	5	GLC
		181,000	0.774	0.135		
		292,000	0.627	0.23		
75	2N	26,000	0.790	0.10	5	GLC
		35,000	0.760	0.13		
		68,400	0.628	0.28		
		68,400	0.606	0.25		
120	0.1	470	0.98	--	1	PSA
		596	0.91			
		1,150	0.86			
		2,380	0.60			
		6,370	0.20			
120	0.1	550	1.04	--	1	PSA
		1,250	0.88			
		2,350	0.64			
120	0.5	560	1.12	--	1	PSA
		1,250	0.84			
		2,480	0.47			
120	2.0	190	1.04		1	PSA
		330	0.97			
		670	0.83			
150	0.1	103	0.95		1	PSA
		190	0.76			
		660	0.28			
150	0.1	10	1.03		0.1	PSA
		13	1.05		0.1	
		335	0.19		0.2	
		350	0.22		0.2	
		550	0.20		1.0	
		510	0.17		0.5	
150	0.1	20	0.88	0.062	0.2	GLC
		100	0.59	0.255	1.0	
		190	0.34	0.395	1.0	
		340	0.17	0.42	1.0	
150	1.0	20	0.73	0.13	0.2	GLC
		110	0.22	0.35	1.0	
		210	0.07	0.25	1.0	
		380	0.01	0.06	1.0	
150	1.0[a]	22	0.71	0.14	0.2	GLC
		43	0.45	0.27	0.2	
		110	0.29	0.36	1.0	
		200	0.13	0.31	1.0	
		360	0.02	0.09	1.0	
170	0.1	0.7	0.90	0.09	0.004	GLC
		1.0	0.89	0.12	0.004	
		8	0.69	0.26	0.016	
		15	0.45	0.35	0.016	
170	0.1	9	0.72	--	0.016	PSA
		9	0.69		0.016	
		16	0.54		0.016	
		24	0.38		0.016	
170	1.0	1.1	0.43	0.23	0.004	GLC
		2.3	0.40	0.25	0.008	
		4.6	0.40	0.26	0.016	

[a] These runs were made with a white liquor of 1.0N effective alkali and 30% sulfidity. The runs at 60 and 75°C were made with a glass flow reactor.

Table II. Kinetic Data for Peeling of Cellobiose in Alkali

Temp., °C	NaOH concn., N	Half-life, millisec
60	2	520,000
	0.02	3,500,000 (4)
75	2	105,000
	0.02	900,000 (4)
120	0.1	3,000
	0.5	1,500
	2.0	1,500
150	0.1	120
	1.0	55
170	0.1	15
	1.0	7 to 11.6

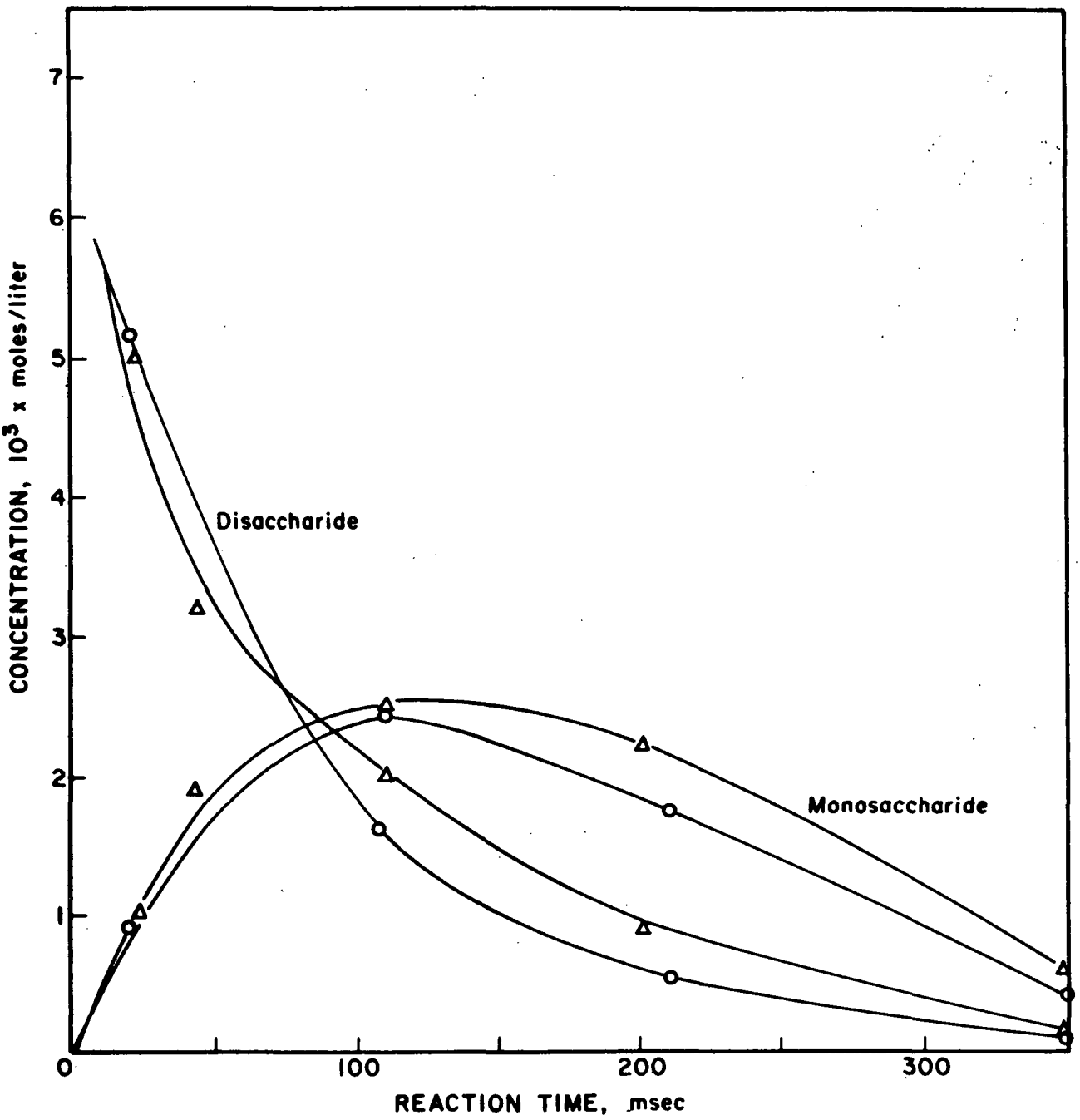

Fig. 1. Reaction of 0.007M cellobiose at 150°C with 1.0N sodium hydroxide (o) and with white liquor of 1.0N effective alkali and 30% sulfidity (Δ). (GLC analysis.)

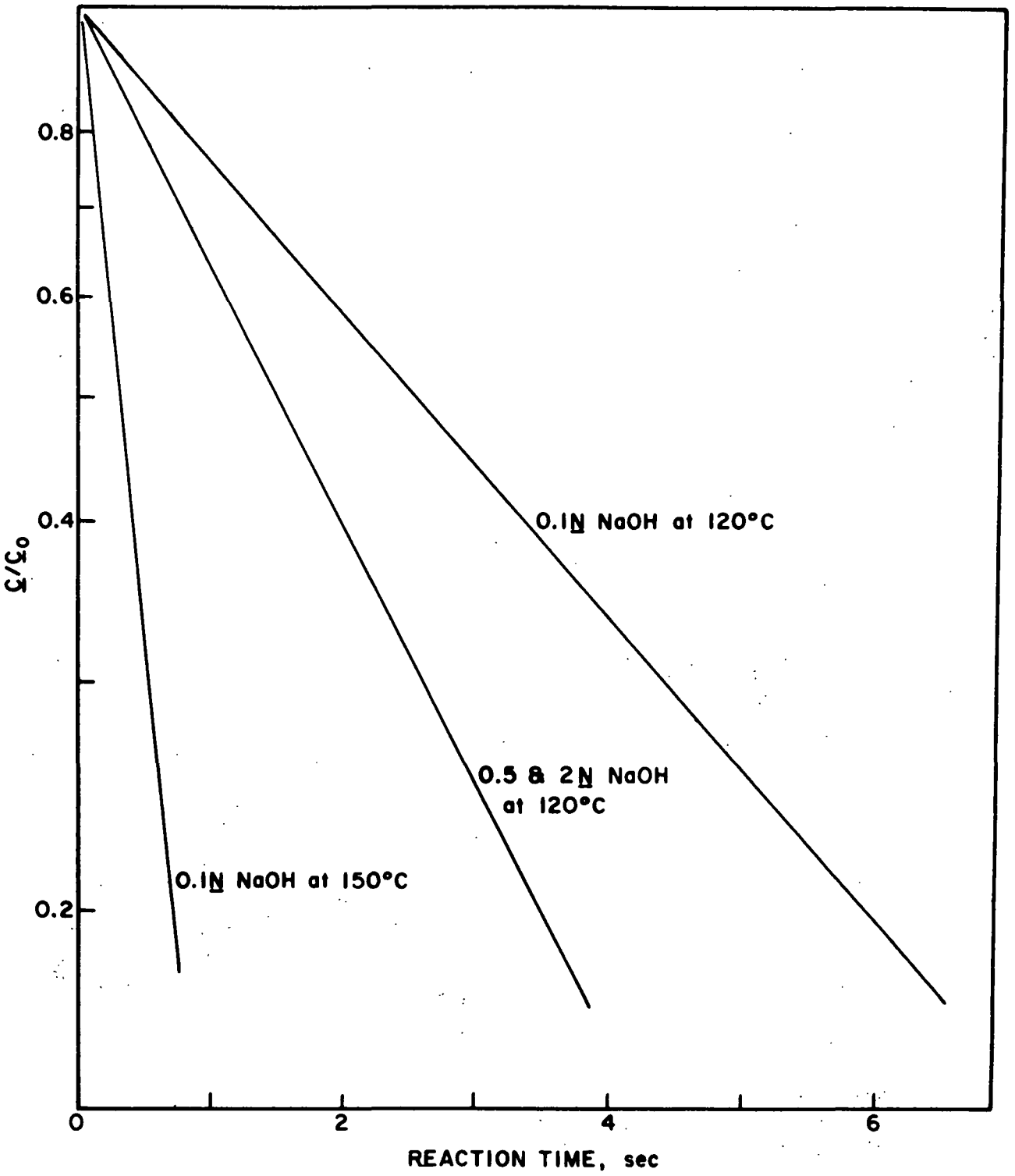

Fig. 2. Comparison of first-order kinetic plots for various reaction conditions, with force-fit through $C/C_o = 1.00$.

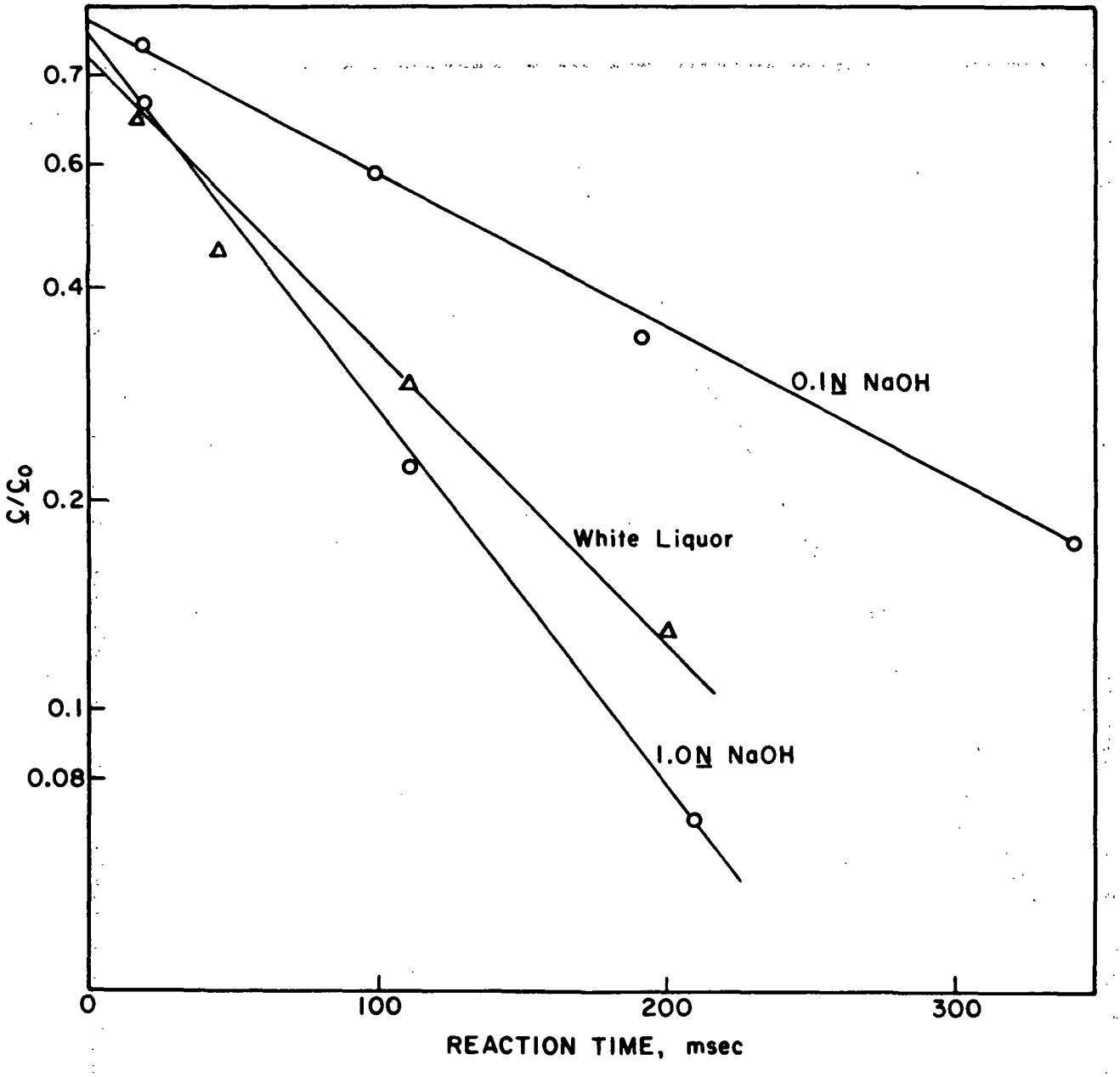

Fig. 3. First-order kinetic plot of disappearance of disaccharides in the reaction of 0.007M cellobiose at 150°C with 0.1 and 1.0N sodium hydroxide and with white liquor of 1.0N effective alkali and 30% sulfidity. (GLC Analysis.)

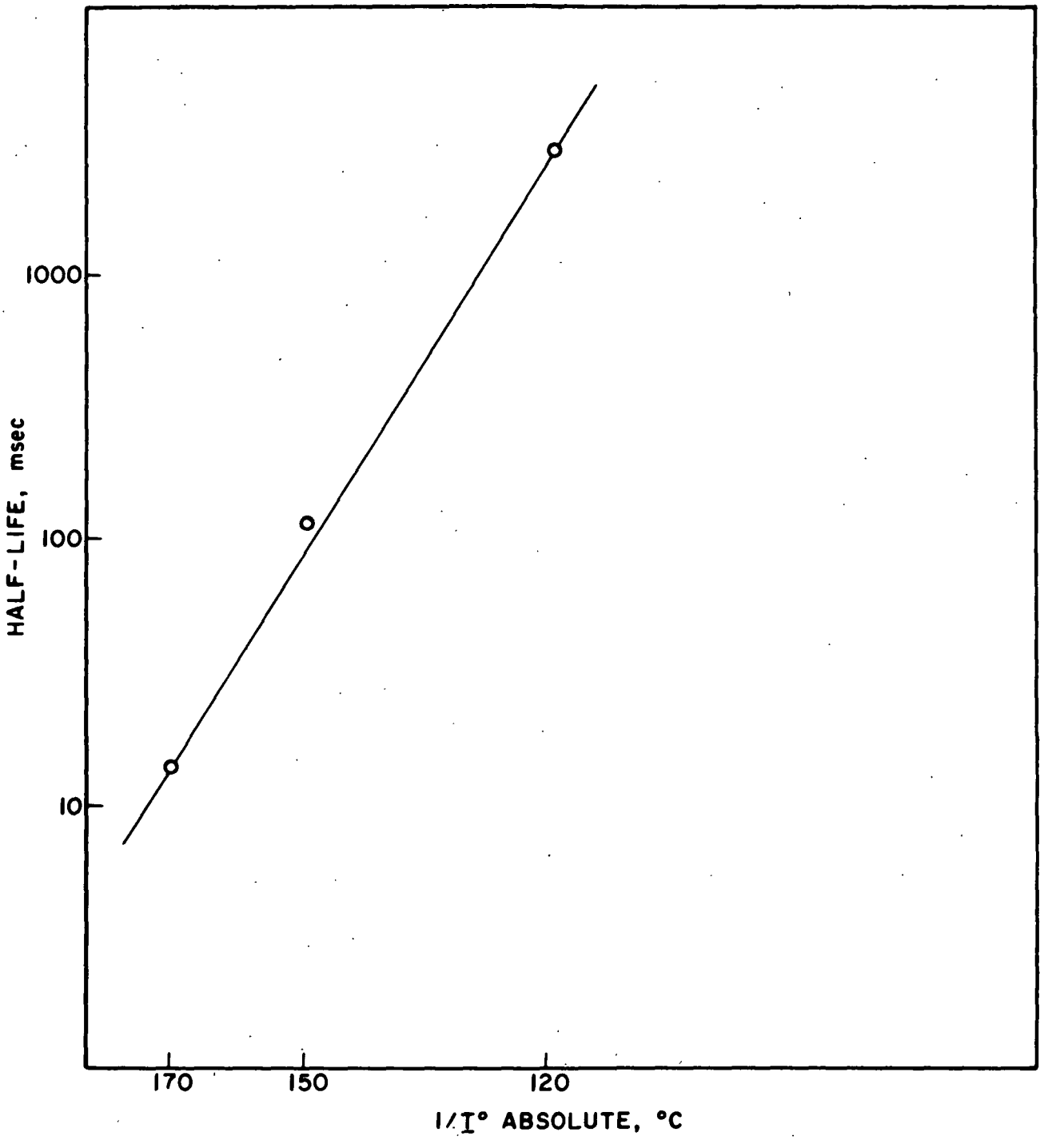

Fig. 4. Relation of kinetic data to temperature. Reaction of 0.007M cellobiose with 0.1N sodium hydroxide.

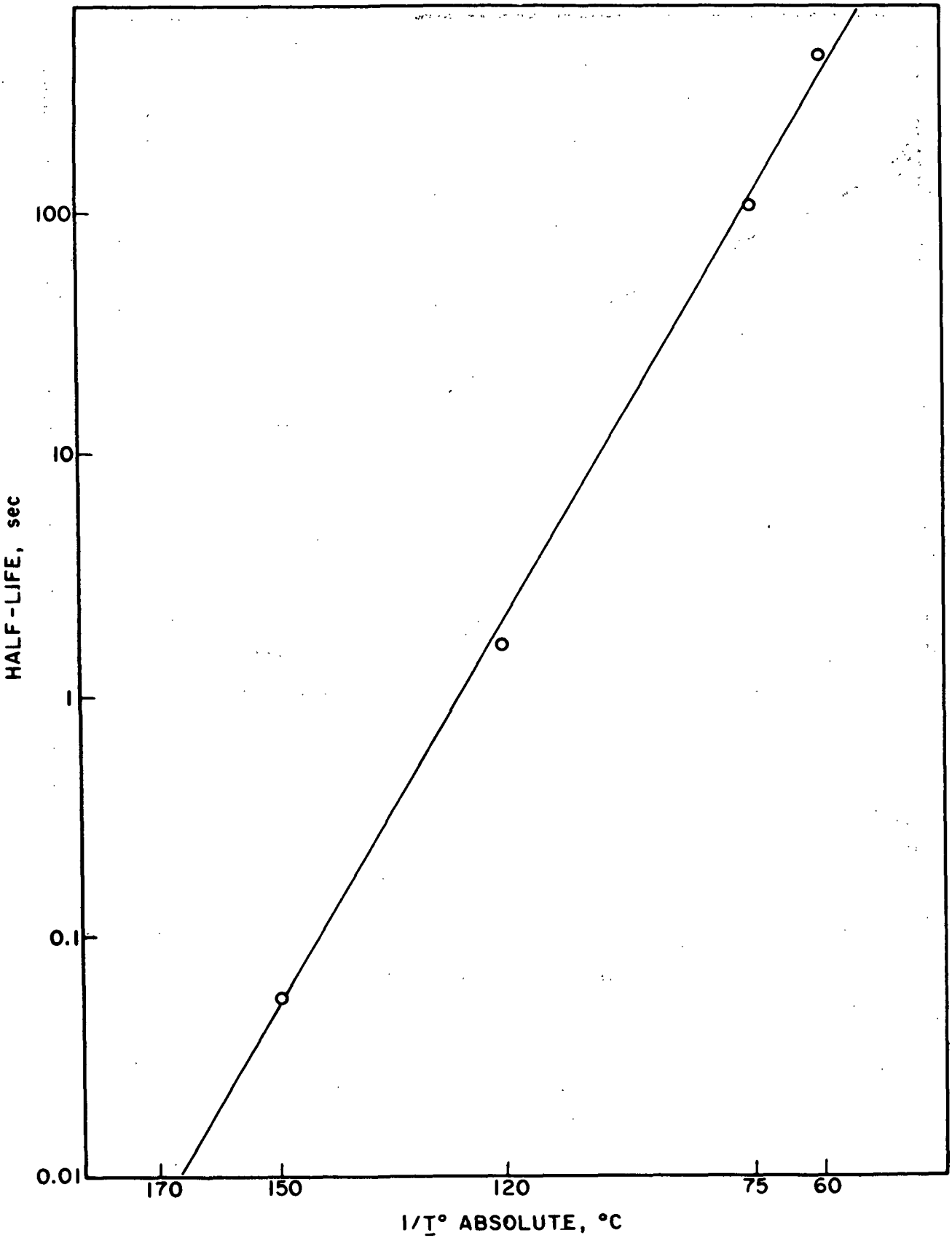

Fig. 5. Relation of kinetic data to temperature. Reaction of 0.007M cellobiose with 0.5N to 2.0N sodium hydroxide.

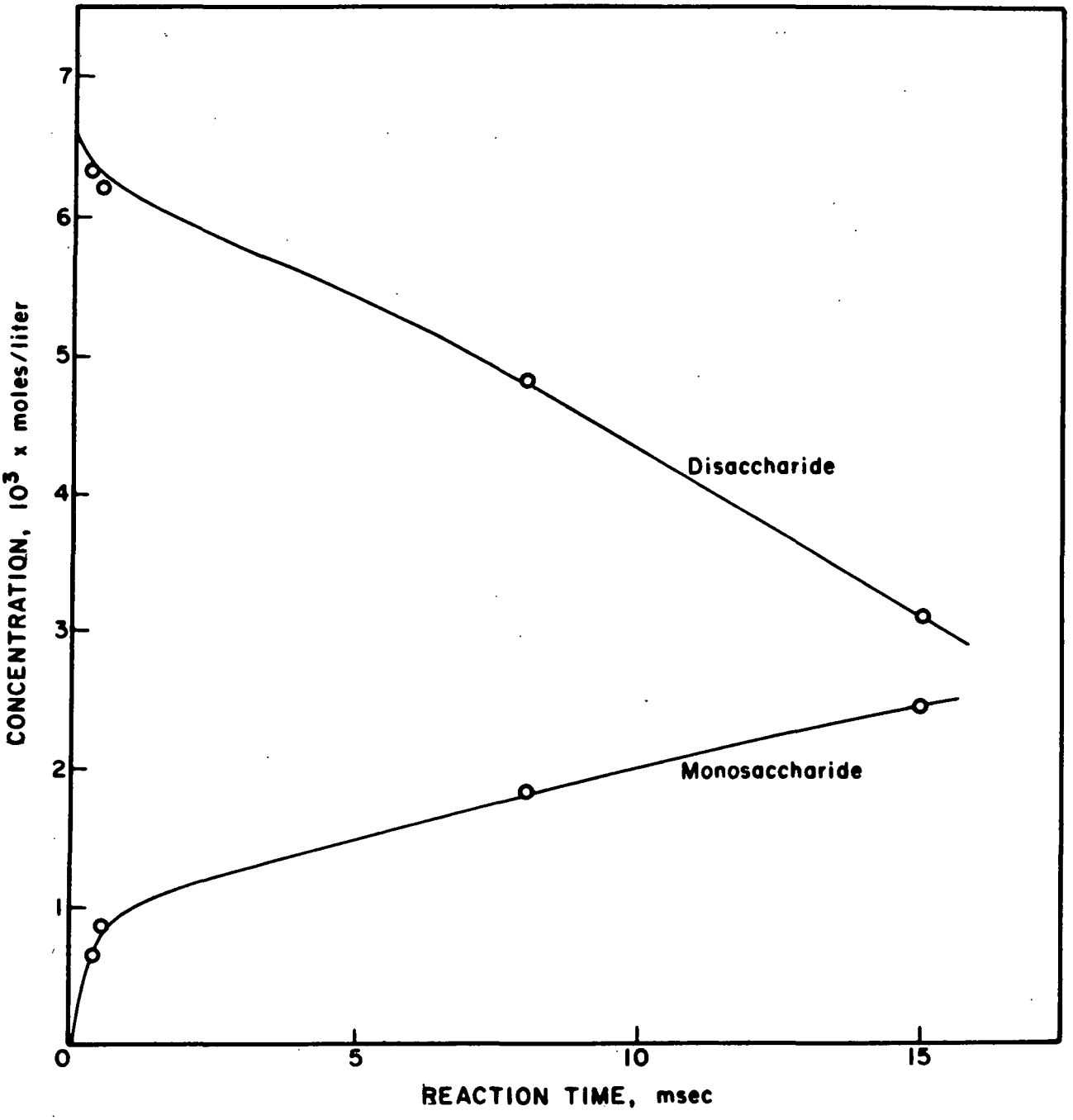

Fig. 6. Reaction of 0.007M cellobiose with 0.1N sodium hydroxide at 170°C. (GLC Analysis.)

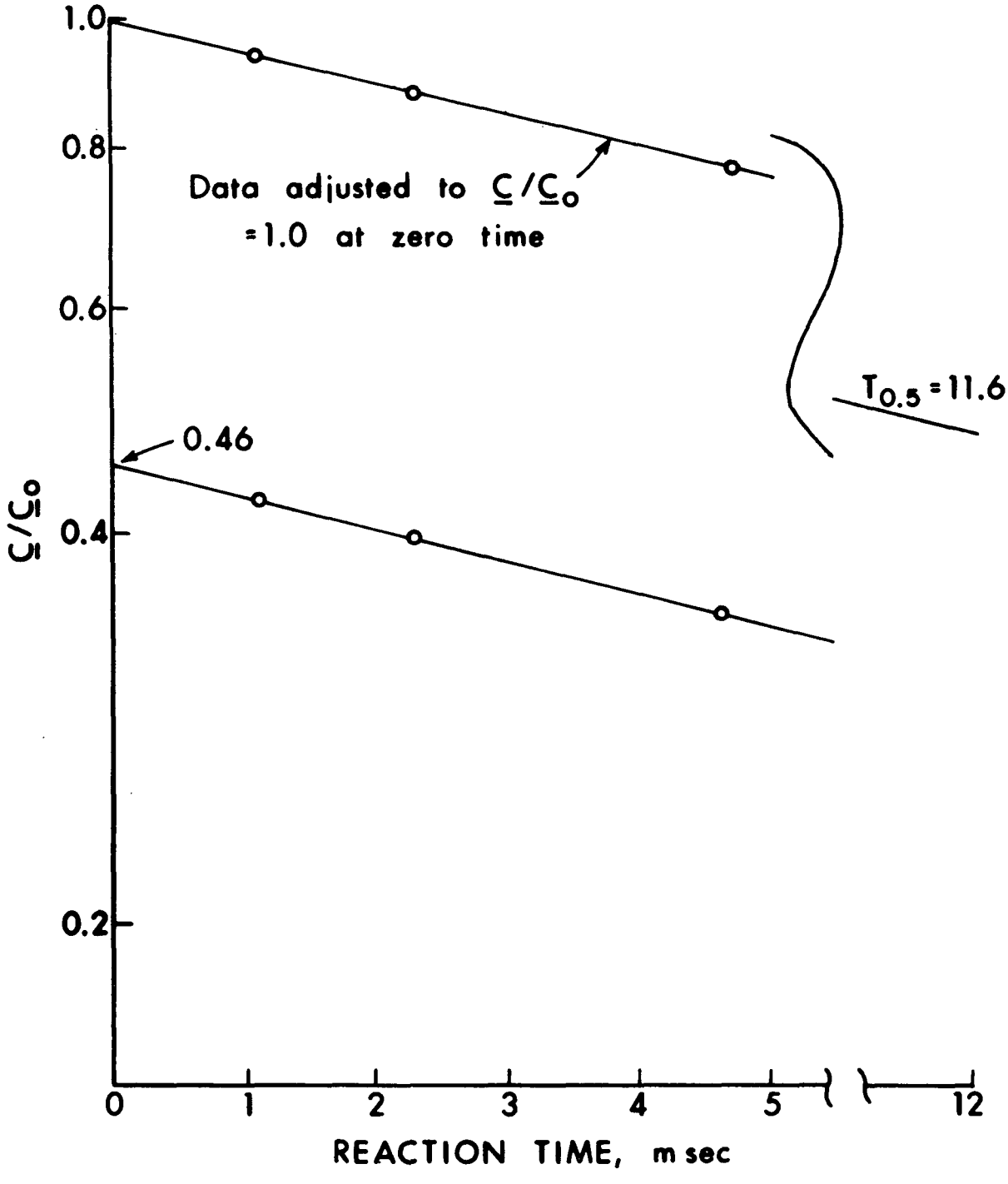

Fig. 7. First-order kinetic plot of disappearance of disaccharides in the reaction of 0.007M cellobiose with 1.0N sodium hydroxide at 170°C. (GLC Analysis.)